Oxidation of the sulphurised dolomite produced in the desulphurisation of the gasification gases ☆

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Keywords:
Calcium sulphide oxidation
Gasification
Dolomite
Coal

A B S T R A C T

Dolomite reacts with H_2S to produce calcium sulphide and has been broadly investigated as a desulphurisation agent due to its low-cost and favourable properties.

Because CaS reacts with water or water vapour in the environment to regenerate hydrogen sulphide and, therefore, disposal is problematic and the chemical cannot be uses as a landfill material. One of the methods used to make this material inert is oxidation to convert calcium sulphide into calcium sulphate or calcium oxide.

In our study, tests were carried out using dolomite from Granada, Spain, that was previously calcined and sulphurised at high temperature with a gas similar to that produced in gasification facilities. To approximate real-scale results, a relatively large amount of substance was used for each sample (100–150 g) and the samples were used in a fixed-bed position.

The influence of different conditions, such as grain size, composition of the oxidation gas, gas velocity, bed length and temperature, was them investigated. The final solid products were characterised by X-ray diffraction and chemical analysis and the CO_2, SO_2, H_2S and COS concentrations in the gases produced during oxidation were analysed by gas chromatography.

The results showed that the most influential factor was grain size and that the best oxidant was O_2 mixed with nitrogen.

The presence of water vapour increases the residual concentration of CaS in the end product, but increased the CaO content

The higher the oxygen concentration and the higher the gas velocity, the lower the residual content of CaS. CO_2 used alone oxidises CaS to produce SO_2 and COS, but at very low rates. It also produces some CS_2. Water vapour used alone can also oxidise the CaS to produce H_2S and SO_2 but also at very low velocity.

At higher oxidation temperature, between 700°C and 850 °C, lesser residual CaS is obtained in the oxidised product.

1. Introduction

During the gasification of coal or its blends with other alternative fuels, sulphur is mainly present in the gas as hydrogen sulphide. The sulphur compound can be eliminated prior to gas combustion in order to comply with legislation in force regarding polluting emissions and specially to avoid damage in turbines during power generation or gas engines. Removal of this compound also serves to reduce corrosion in general and, in the chemical industry, to avoid damaging certain catalysts.

The scrubbing of sulphur from the gas stream has been broadly studied by using different desulphuring agents, such as amines used by Elcogas IGCC in Spain. However, this option requires lowering the gas temperature, a step that involves energy losses.

Some sorbents capable of capturing H_2S at high temperatures, including various metal compounds, have been studied [1,2]. Sorbent regeneration without significant degradation over a certain number of cycles is very important. With this idea in mind a number of Zn compounds [3–6], Mn and Cu compounds and blends [7–9], and several Fe compounds [10] have been studied. The main problem is the duration of a sufficient number of cycles without degradation.

One extremely cheap oxide, CaO, has been studied as it would make reuse unnecessary. Its principal carries are two abundant minerals, calcite and dolomite. The direct addition of this oxide or calcite or dolomite in the gasification bed during the gasification of coal or other alternative fuels has also been investigated [11] not only to obtain a clean gas, but also to produce hydrogen [12]. The absorption of H_2S contained in gasification gases to remove it from this gas by means of these oxides has also been studied [13–20].

Table 1
Chemical reactions.

Number	Reaction	ΔH^0 kJ mol^{-1}
(1)	$H_2S + CaO \leftrightarrow CaS + H_2O_{(g)}$	−59.2
(2)	$CaS + 3/2O_2 \leftrightarrow CaO + SO_2$	−458.9
(3)	$CaS + 2O_2 \leftrightarrow CaSO_4$	−952.2
(4)	$CaS + CO_2 \leftrightarrow CaO + COS$	+93
(5)	$CaS + 3CO_2 \leftrightarrow CaO + 3CO + SO_2$	+390
(6)	$CaS + 3H_2O \leftrightarrow CaO + 3H_2 + SO_2$	+266.6
(7)	$COS + 2O_2 \leftrightarrow CO_2 + SO_2$	−552
(8)	$H_2S + 3/2O_2 \leftrightarrow H_2O + SO_2$	−515.2
(9)	$COS + H_2O_{(g)} \leftrightarrow H_2S + CO_2$	−33.6
(10)	$CO_2 + H_2S \leftrightarrow COS + H_2O_{(g)}$	+33.6
(11)	$CO_2 + 2H_2S \leftrightarrow CS_2 + 2H_2O_{(g)}$	+68
(12)	$2CaS + CO_2 \leftrightarrow CS_2 + 2CaO$	+186.42
(13)	$COS + CaS \leftrightarrow CS_2 + CaO$	+93.4
(14)	$CaS + 3CaSO_4 \leftrightarrow 4CaO + 4SO_2$	+1020.8
(15)	$CaS + 4CO_2 \leftrightarrow CaSO_4 + 4CO$	+179.8
(16)	$CaS + 2CO_2 \leftrightarrow CaCO_3 + COS$	−419.9

Calcium oxide is effective in absorbing H_2S from the gasification gases according to the reaction (1) given in Table 1.

However, a problem arises regarding how to handle this calcium sulphide product which reacts with water or water vapour and regenerates H_2S as an inverse reaction to the sulphidisation reaction (1). This phenomenon has been investigated by some authors [21] who have demonstrated the reaction of the compound with the atmospheric water vapour o the superficial water, a property which makes it unsuitable for landfill material, an option that would have been the cheapest alternative.

Several methods to convert this product into a "non-hazardous" product or to obtain some use from it have been investigated. One of these involves reacting CaS with water and MDEA (Methyldiethanolamine) to recover H_2S at ambient temperature [22].

As calcium oxide is used as an absorbent at high temperature, research on its stabilisation at high temperature is also interesting. The majority of the studies carried out involve the oxidation of CaS. One of these attempts to recover CaO, to reuse it [23] preventing the sulphate formation. Unfortunately this reaction must be performed at very high temperatures (above 1400 °C) and the retention capacity of H_2S quickly decreases after a few cycles.

Others researchers have studied this oxidation at lower temperatures with the intention of oxidise calcium sulphide and turning it into a mixture of calcium sulphate and calcium oxide, using for their works thermogravimetric analysis equipment or differential reactor equipment that requires small samples (<1 g) and small grain size with the main aim of measuring kinetic parameters [24–26].

Wu et al. [27] also used small amounts of calcium sulphide and claimed to have found a synergistic effect between H_2O and O_2 during high-temperature oxidation.

The effect of gaseous products given off by a part of one particle into other parts of the same particle due to gaseous products given off during CaS conversion ('intraparticle' reactions) has been demonstrated by some of these researchers despite using smaller grain sizes and smaller quantities of the substance [21,25]. Is evident that is possible the action of gaseous product released by one particle on other particle ('interparticle' reactions). Undoubtedly, highly significant 'intraparticle' and 'interparticle' effects would result whenever larger grain sizes and larger quantities of substance are used to form a bed of considerable length compared with grain size.

In the study described herein, the product chosen for H_2S absorption was dolomite as it works well under calcining (1173 K) and non-calcining (1123 K) conditions according to previous studies by Adanez [18,19], Pinto et al., [20] and Álvarez-Rodríguez and Clemente-Jul [28].

Furthermore, all the aforementioned studies on CaS oxidation have been carried out with purchased or prepared CaS. However, when dolomite is used as a desulphuring agent, the calcined product is a blend of CaO and MgO and forms a blend of CaS and MgO after its sulphurisation. Due to this fact, this product must be obtained in the laboratory itself because it is not a commercial product.

A large amount of product has also been used (100 g or 150 g of dolomite, bed lengths of 11.4 cm and 17 cm, respectively) in a fixed-bed arrangement to more closely approximate industrial conditions because there are 'interparticle' reactions as well as 'intraparticle' reactions, since the gases given off by a particle can react with other particles encountered along the way. These reactions are minimised in thermogravimetric analysis carried out with very small mounts of substance.

The effect of grain sizes from 0.4 to 2 mm has also been studied to show the influence of intraparticle reactions.

Another problem is that the molar volume of calcium sulphate (46.0 cm^3 mol^{-1}) is higher than that of calcium sulphide (28.9 cm^3 mol^{-1}) or the initial calcium carbonate (36.9 cm^3 mol^{-1}) [24]. Therefore, the pores of the particles produced by dolomite calcination could become clogged or covered during the oxidation reaction and eventually hinder complete oxidation [21,24–26].

Oxidation using oxygen can be formulated as reactions (2) and (3) (Table 1).

It is known that calcium sulphide can also be oxidised by carbon dioxide [25,26] and by water vapour [26,27]. In fact, various reactions have been proposed as (4)–(6) (Table 1). For instance, one of these reactions (4) is the inverse of COS absorption reaction by CaO, that takes place in the gas desulphurisation process. Other reaction is the inverse of H_2S absorption by CaO (1).

These oxidant substances (O_2, H_2O vapour and CO_2) are present in flue gases from combustion processes at various relative proportions, depending on the fuel used and the degree to which combustion is complete. For this reason, a gas blend that could be considered as an example of gases emitted by combustion processes has been used and the influence of each gas has been investigated.

In this investigation, which uses a relatively large amount of substance, several other factors were to be considered because, after the initial moments of oxidation, there are (at least superficially) amounts of CaO that may react with some of the gases present in the gas stream or given off in the previous section of the sample, depending on its concentration and affinity, which also depends on temperature.

The temperature of gases that come into contact with the calcium sulphide has also been kept constant, but reactions (2) and (3) are very quick (see below) and exothermic. Therefore, the bed temperature increases considerably and consequently the reactions do no take place under isothermal conditions.

If oxygen is present together with CO_2 and H_2O, any carbonyl sulphide formed by reaction (4) can react with oxygen according to the exothermic reaction (7) that modifies the gas composition and also generates more heat.

COS can also react with CaO by the reverse of reaction (4) and the newly formed CaS can react.

When water vapour is present, one of the possibilities is that hydrogen sulphide is formed by the reverse of reaction (1). This H_2S can react with oxygen, leading to the exothermic reaction (8) (Table 1), which also modifies the gas composition and generates more heat.

Another possible reaction between COS and H_2O is (9) (Table 1), a hydrolysis reaction that reduce the presence of COS.

Ishida [23] also suggest the occurrence of the reactions (10) and (11). In this study these reactions are unlikely because there is lit-

tle or no H_2S in gases. However, COS is detected (and in especially case also CS_2) which shows that reactions (4) and (12) can occur.

The reaction (12) can be considered as the sum of reaction (4) plus reaction (13).

Another possible reaction considered by various authors and studied by Kamphuis et al., [29] is (14) (Table 1). This is a reaction between solids and the author concludes that it takes place when a blend of these components is heated in an inert atmosphere at a temperature higher than 1100 K. Depending on the amounts initially present, the reaction can attain near complete conversion.

During the oxidation of sulphurised dolomite, SO_2 is produced by reactions (2),(5) and (6). This gas cannot be emitted to the atmosphere, but can be used to produce sulphuric acid or can be converted in calcium sulphate by using methods similar to those used in the treatment of gases given off in combustion plants to generate power. There are also several studies on SO_2 elimination such as [30] that uses a dual bed of potassium-containing coal pellets and calcium-containing pellets. Others use a product based on Fe/AC (AC: active carbon/coke) that can be regenerated [31] or another study that uses a Mo- and Co-doped V_2O/AC sorbent [32].

2. Experimental

To simulate a possible industrial application, this investigation used a recent calcium sulphide produced "in situ" (according the procedure described in Álvarez-Rodríguez and Clemente-Jul [28]) instead of pure calcium sulphide acquired from a supplier. For the production of this calcium sulphide, dolomite from the province of Granada, Spain, was used. Their X-ray diffractogram and analysis are shown in Fig. 1 and Table 2, respectively. The analysis show that their composition is very close to the mineral theoretical composition.

This dolomite can decompose completely at 850 °C and be transformed in calcium and magnesium oxides: Fig. 2 shows the thermogram for dolomite in a nitrogen atmosphere (40 cm^3/min) with a temperature gradient of 10 °C/min up to 850 °C, followed by constant temperature thereafter. When the temperature reach 850° C continues the lost of mass (CO_2 emission), but with the temperature stabilised at 850 °C, in about 200s the weigh stabilised and reach the theoretical for the total decomposition of the dolomite that is corroborated by X-ray diffraction. The thermobalance used was a Setaram–Labsys.

Table 2
Granada dolomite analysis.

Element	Content (%)
CaO	30.51
MgO	21.68
Fe_2O_3	0.06
MnO	0.007
TiO_2	0.006
SiO_2	0.1
Al_2O_3	<0.1
K_2O	<0.1
Na_2O	<0.1
P_2O_5	<0.05
Insoluble	0.20
Loss on ignition	47.53

The calcined dolomite (a mix of CaO and MgO) is sulphurised using a blend of gases with H_2S until the outlet gas composition stabilises and has virtually the same H_2S content as the inlet gases. Conversion with regard to calcium with this procedure is about 97–99%.

This sulphidisation is carried out with the same equipment used for oxidation. In the case of oxidation, the inlet gas composition is changed after 'scrubbing' the reactor interior with pure nitrogen. The equipment used was a Kanthal vertical tube reactor with a length of 1.6 m and inner diameter of 27 mm which passes, in its central part, through a furnace with an inner length of 600 mm. This equipment was previously described by Adánez et al. [17,19] and Álvarez-Rodríguez and Clemente-Jul [28].

To carry out the oxidation, the sample is initially stabilised at 850 °C or 700 °C using a nitrogen stream at the same velocity as the oxidising blend to control the furnace resistor temperature. A temperature of 850° was chosen because dolomite sulphidisation works very well at this temperature [17,19,28]. To study the influence of temperature, other tests have been carried out using 700 °C [25].

Oxidation is then produced by injecting the oxidant blend (and modifying the nitrogen flow to maintain the total flow of gas) and the inlet gas velocity is kept at 10 l/min and 5 l/min (29.1 and 14.5 cm s^{-1}), considered by various authors as a typical case of plug flow [15]. All gases are controlled by specific mass flow controllers and water vapour is obtained by complete evaporation of a constant flow rate of water controlled by a mass flow controller

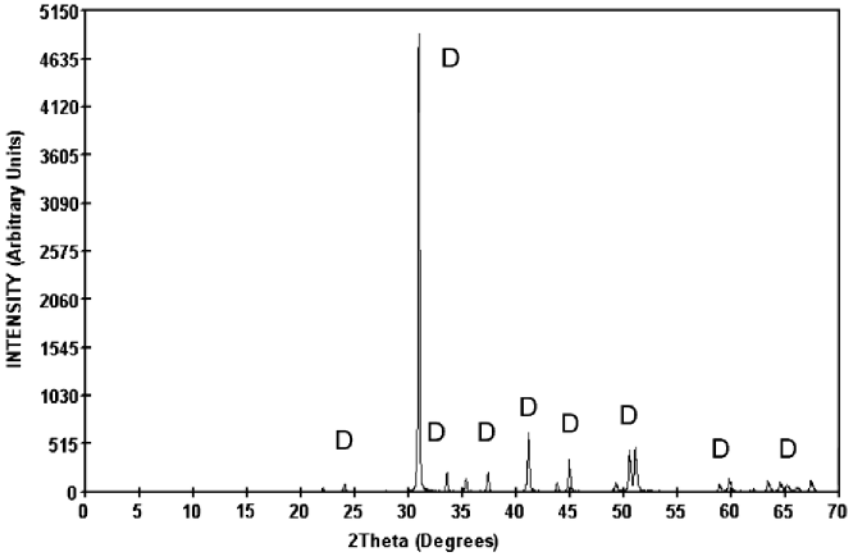

Fig. 1. Diffractogram of Granada dolomite used (D: dolomite).

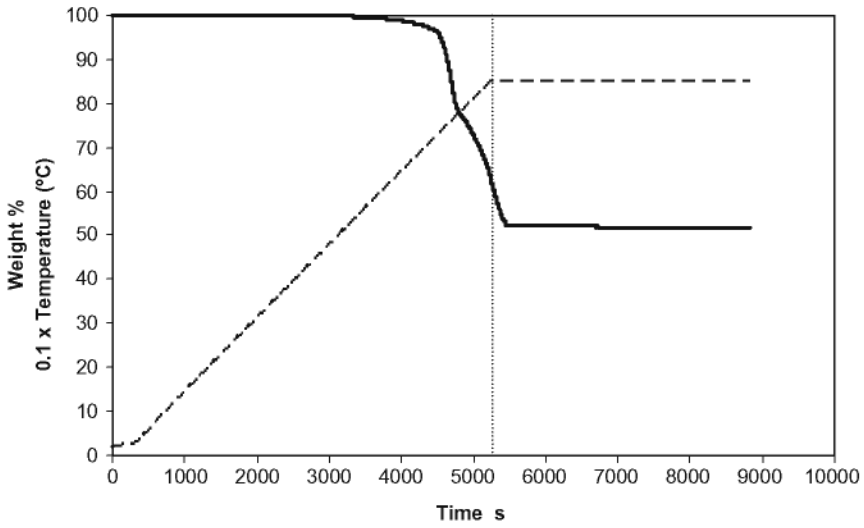

Fig. 2. Thermogram of the dolomite used (– weight, –– temperature).

and evaporator mixer. The certified deviations of the mass flow controllers (for flows measured under 75% of the fond scale) were lower than 0.3% of FS (±0.03 l/min for 10 l/min).

The gases are introduced at the top of the reactor to ensure that they move below through the material bed, oxidising the material. The gas temperature is controlled in the area where the gases come into contact with the sulphurised material. Oxidation is assumed to be complete when the SO_2 content of the outlet gas is less than 20 ppm.

Once oxidation is complete and after scrubbing with nitrogen to try to eliminate the physical absorbed gases, power to the furnace is cut off, the furnace is opened and the reactor is allowed to cool in a nitrogen atmosphere. Once cooled, the reactor is opened and the substance is collected.

The different gas blends used in the oxidation were: pure nitrogen plus oxygen, nitrogen plus carbon dioxide, nitrogen plus water vapour and nitrogen with various levels of carbon dioxide, water vapour and oxygen. The purpose of this choice was to analyse the possibility of using as oxidants the gases produced in combustion plants fired by various types of fuels.

The column of initial substance (dolomite) and later the bed to be oxidised (CaS plus MgO) in a fixed-bed arrangement is formed with 100 g or 150 g of granulometrically classified dolomite, as 0.4–0.5 mm, 0.71–1 mm or 2–2.5 mm to determine behaviour according to grain size. The use of 100 g leads to a bed length of 11.4 cm and 150 g leads to a bed length of 17 cm.

The oxidation gases given off by the reactor at the bottom flow through a coolant to separate any water used in the oxidant blend before the gases are analysed (for H_2S, COS, SO_2 and CO_2) in a Varian CP-4900 Micro-GC chromatograph fitted with a 10 m Porabond Q column module and Thermal Conductivity Detector that takes a sample every 5.7–6 min. There is also another DMD detector that is more sensitive to sulphur compounds and can be used to tray and detect other sulphur compounds, in very low quantities, such as CS_2.

In experiments in which only oxygen (plus nitrogen) was used as an oxidant gas, oxygen was analysed using a TESTO 350 oxygen analyser. The oxidised sample was collected and analysed by X-ray diffraction (Phillips PX-1710) and wet chemical analysis to determine $CaSO_4$ and CaS content.

Tests were carried out at atmospheric pressure with a slight overpressure of approximately 0.1 bar to simulate the pressure required for gas circulation. The total pressure was 0.11 MPa.

The conditions used in each test are shown in Table 2. Along with the tests listed, other duplicate tests were carried out to ensure results. The maximum deviation in chemical analysis is ±0.05 by values of the order of 50%, and ±0.01 by values lower than 1%.

3. Results and discussion

3.1. Oxidation with a blend of N_2 and O_2 only

3.1.1. Influence of grain size and bed length

When operating as described in Section 2, dolomite sulphidisation is virtually complete (97–99%) when a grain size of 2–2.5 mm is used. This grain size is the bigger size used in this work and by consequence the most difficult to sulphurise under different conditions. Fig. 3 shows the X-ray diffraction of sulphurised dolomite. The calcium sulphate or calcium oxide lines are absent and only de CaS (oldhamite) and MgO (periclase) lines can be seen.

Fig. 4 shows the plots of the variation of SO_2 content in the outlet gases with the time for various oxidation tests carried out using as oxidising gas a blend of 96% N_2 and 4% O_2 (tests 1, 6, and 11, Table 2). The gas velocity is of 29.1 cm s^{-1} and the sulphurised dolomite to be oxidised has grain sizes of 0.4–0.5 mm, 0.71–1 mm and 2–2.5 mm. The weight of the initial dolomite in the samples (previously to their calcination and sulfurisation) was 100 g (11.4 cm bed length).

The analysis of oxidised samples is presented in the first three rows of Table 4. The table shows that residual CaS content increases with grain size, indicating that this factor has significant major influence. This occurs, as mentioned above, because the molar volume of $CaSO_4$ is higher than that of the initial carbonate molecule. The formation of this compound tends to clog pores and hinder oxidant penetration and therefore oxidation progress. This effect is more significant as grain size increases and becomes more difficult to reach the middle of the grain.

Fig. 5 shows the X-ray diffractograms of two extreme cases (0.4–0.5 mm and 2–2.5 mm), showing the increased importance of the CaS lines (Oldhamite, O). It is clear that the main or more intense line of CaS, which overlaps with a $CaSO_4$ line (Anhydrite, A) is higher with 2–2.5 mm than 0.4–0.5 mm; the opposite occurs with regard to the CaO line.

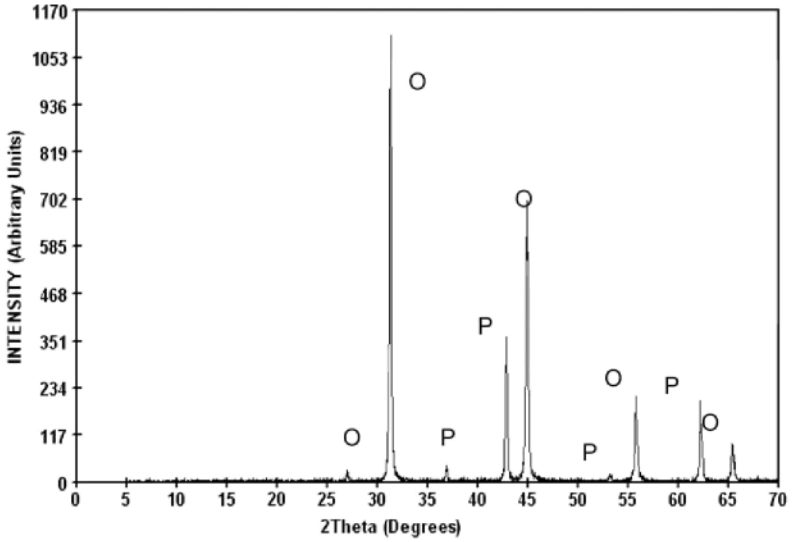

Fig. 3. Diffractogram of sulphurised Granada dolomite (O: oldhamite, P: periclase).

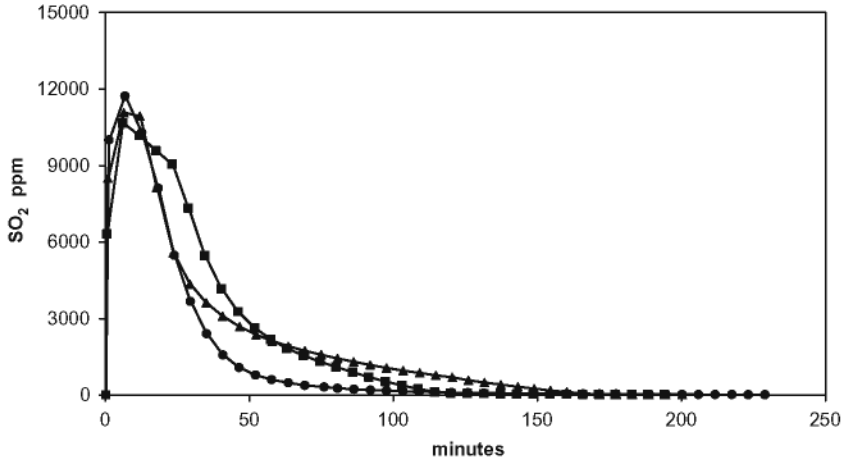

Fig. 4. SO_2 content in the outlet gases during oxidation at 850 °C, 4% O_2, 11.4 cm bed, 29.11 cm s^{-1} gas velocity: tests 1 (▲: 0.4–0.5 mm), 6 (■: 0.71–1 mm) and 11 (●: 2–2.5 mm).

In fine grain sizes, the large area increases the reaction rate and increases SO_2 production by oxidation and therefore CaO content. This SO_2 quickly comes into contact with the gas stream and is diluted in this gas stream, thereby hindering adsorption by the outer layer of CaO, previously formed on others grains. In the larger grains and because oxidation should progress in more internal areas of the grain, the SO_2 produced needs to pass through more layers of the grain to go out. Because oxygen and CaO are present in these areas (previously oxidised), $CaSO_4$ may form as result, which tends to clog the pores due to a higher molar volume and stop any further oxidation earlier due to diffusion difficulties. This is a typical case of 'intraparticle' influence that increases with grain size.

This fact is not coincident with the fact than in the desulphurisation process the grain size may be bigger to obtain the maximum transformation rate of the calcined dolomite [28] using a fixed bed disposition. It is due that in the desulphurisation process there is not the problem of pore clogging into the calcined dolomite grain, but lower grain sizes results in greater grain packing in a compact bed of calcined dolomite grains, thus creating preferential paths for the gas and delaying H_2S absortion. In the oxidation process the better grain size for the oxidation is the 0.4–0.5 mm, the smaller used. In the desulphurisation process [28] the best gain size is 2–2.5 mm, the bigger used.

To study the influence of bed length, a test was carried out with grain sizes of 2–2.5 mm (because it is the most sensitive size among those studies, due to containing more residual CaS) using 150 g of dolomite (17 cm bed length) instead of 100 g (Table 3). When compared with the 100 g test, a small increase in residual CaS is seen (4.55% vs. 4.32%); this reveals that this parameter has little influence and shows that a little higher residual CaS content is obtained with higher bed lengths. This is due to the fact that the SO_2 gas produced (but diluted into the gas flow) circulates for longer among grains partially oxidised with CaO and has more opportunity to react with CaO and O_2 to produce more $CaSO_4$, giving rise to more pore clogging. This is a typical case of 'interparticle' effect.

According to [29], reaction (14) (Table 1) can occur at the temperature used (850 °C) but virtually No SO_2 (<20 ppm) is given off by the end of the test and residual CaS and $CaSO_4$ are present, showing that this reaction is virtually unimportant under the conditions used.

For a given temperature (all other conditions being identical), the $CaO/CaSO_4$ ratio is clearly lower for higher sizes (2–2.5 mm)

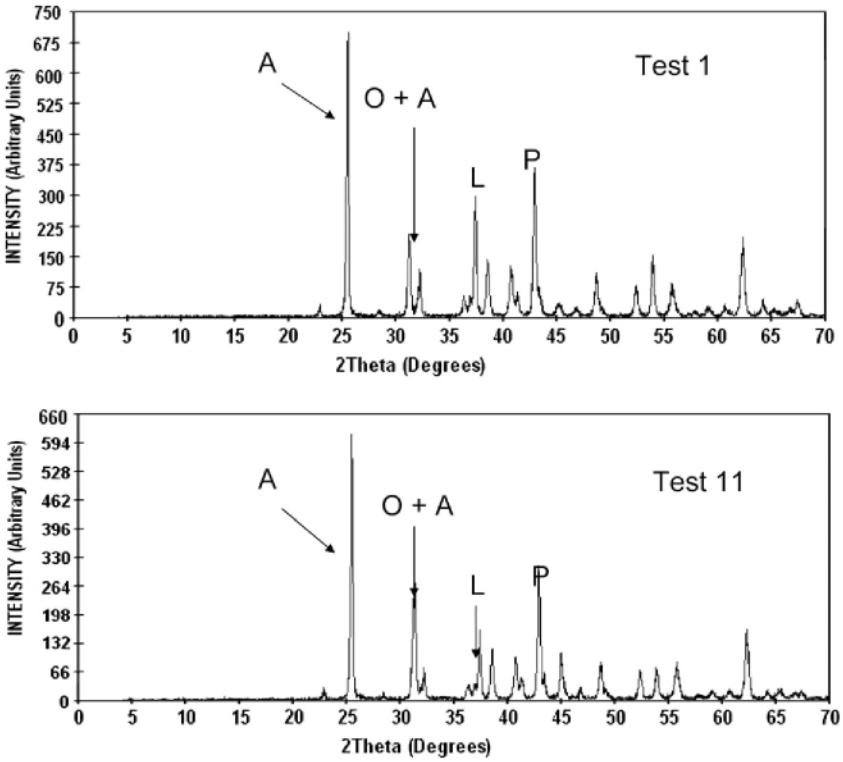

Fig. 5. X-ray diffractogram of oxidized products (4% O_2) of test 1 (in top position) (0.4–0.5 mm), test 11 (in bottom position) (2–2.5 mm); A: anhydrite, L: lime, O: oldhamite and P: periclase.

Table 3
Test conditions for sulphurised dolomite oxidation (nitrogen as balance gas).

Test	Size (mm)	Bed length (cm)	Gas velocity (cms^{-1})	Tempera. (°C)	O_2 (%)	H_2O (%)	CO_2 (%)
1	0.4–0.5	11.4	29.11	850	4	–	–
2	0.4–0.5	11.4	29.11	850	4	7	13
3	0.4–0.5	11.4	29.11	850	1st No, 2nd 4	7	13
4	0.4–0.5	11.4	29.11	850	1st No, 2nd 4	–	17
5	0.4–0.5	5.7	29.11	700	4	–	–
6	0.71–1	11.4	29.11	850	4	–	–
7	0.71–1	11.4	29.11	850	4	7	13
8	0.71–1	11.4	29.11	850	2	7	13
9	0.71–1	17	29.11	850	4	15.6	7.8
10	0.71–1	11.4	29.11	850	1st No 2nd 4	20	–
11	2–2.5	11.4	29.11	850	4	–	–
12	2–2.5	11.4	14.55	850	4	–	–
13	2–2.5	11.4	29.11	850	4	7	13
14	2–2.5	17	29.11	850	4	–	–
15	2–2.5	11.4	29.11	700	4	–	–
16	2–2.5	11.4	29.11	850	8	–	–
17	2–2.5	11.5	29.11	850	2	–	–
18	2–2.5	11.5	14.55	850	–	–	21
19	2–2.5	11.5	29.11	950	4	–	–

Table 4
Oxidation with a mix of O_2 and N_2: influence of grain size, temperature, bed length and oxygen partial pressure (oxygen content).

Test	Size (mm)	Bed length (cm)	Gas veloc. ($cm\ s^{-1}$)	O_2 (%)	Tempera. (°C)	CaO (%)	$CaSO_4$ (%)	CaS (%)	$CaO/CaSO_4$
1	0.4–0.5	11.4	29.11	4	850	14.76	57.09	0.45	0.258
6	0.71–1	11.4	29.11	4	850	15.14	56.51	0.51	0.268
11	2–2.5	11.4	29.11	4	850	10.18	58.5	4.32	0.174
14	2–2.5	17	29.11	4	850	8.68	60.22	4.55	0.144
15	2–2.5	11.4	29.11	4	700	4.14	47.58	20.07	0.087
5	0.4–0.5	5.7	29.11	4	700	12.12	54.43	5.57	0.223
19	2–2.5	11.4	29.11	4	950	17.61	27.46	21.95	0.641
12	2–2.5	11.4	14.55	4	850	7.94	57.61	7.53	0.138
16	2–2.5	11.4	29.11	8	850	16.08	53.2	2.23	0.302
17	2–2.5	11.4	29.11	2	850	7.48	56.55	8.92	0.132

than for 0.71–1 mm, showing the effect of clogging o covering of pores. When gain sizes of 0.4–0.5 mm and 0.71–1 are compared, this does not occur and may be explained by greater packing and compactness in the case of the 0.4 mm grain size that causes more preferential pathways to circulate the gas as shown in the case of sulphidisation [19,28].

3.1.2. Influence of temperature

Qiu et al. [25] concluded that temperature significantly affects CaS particle oxidation over the entire range of pressures tested in that study and that the level of CaS conversion to $CaSO_4$ increased notably with temperature between 700 °C and 900 °C. Test 15 (2–2.5 mm, 4% O_2, 96% N_2, 29.11 cm s^{-1} gas velocity), Table 4, was carried out at a gas inlet temperature of 700 °C instead of 850 °C (test 11) and showed that residual CaS increased notably (20.07% vs. 4.32%) and that $CaSO_4$ content is lower (47.58% vs. 58.5%). This clearly shows the influence of temperature.

Another test (test 5, Tables 3 and 4) with 50 g and a particle size of 0.4–0.5 mm showed how a high residual amount of CaS (5.57%) is left behind despite lower grain size and shorter bed length. This amount was significantly higher than in the test at 850° with 100 g of dolomite (0.45%) also shown in Table 4.

These results are consistent with the observations by García-Calzada et al. [33] on the calcium sulphide stabilisation due to air heating. Those authors concluded that the best range of temperature was between 800 °C and 870 °C. Those authors concluded that the best range of temperatures was between 800 °C and 870 °C. They claim also a relationship between a high conversion to sulphate and virtually zero emission of SO_2, but this is not in our case.

3.1.3. Influence of gas velocity for oxidation and concentration of O_2

All factors that favour contact between SO_2 produced by oxidation reactions (principally reaction (2)) and CaO previously produced lead to an increase in residual CaS due to increased formation of surface $CaSO_4$ that increased the effect of pore clogging due to the clogging effect of this compound. Table 4 shows the results of various tests with two oxidation gas velocities and three oxygen concentrations. When the results shown in Table 4 are compared, an increase in residual CaS can be seen at lower velocities (test 12 vs. test 11) and at lower oxygen concentrations (test 11 vs. test 16). These results are consistent with [25] who showed that increased O_2 partial pressure results in increased oxidation rate, at least initially.

Comparing test 11 with test 12 in Table 4, lower gas velocity can also be seen to reduce $CaO/CaSO_4$ ratio, showing how the contact time between gas and solid enhances sulphate formation.

Fig. 6 contains plots for SO_2 release at oxygen concentrations of 4% and 8% in the oxidation gas under otherwise equal conditions (gas velocity 29.11 cm s^{-1}, grain size 2–2.5 mm and bed length 11.4 cm). Oxidation rate increases notably at higher oxygen content or concentration levels, thereby increasing the amount of SO_2 in the outlet gases (higher area), consistent with the higher CaO content in the end product.

This effect of gas velocity cannot be clearly separated from the temperature effect in these test carried out with a large amount of substance. This is because any oxidation reactions (2) or (3) are highly exothermic and an increase in gas velocity at the same oxygen concentration (4%) increased O_2 availability per unit time and increases temperature. The same occurs when O_2 content or concentration increases and the inverse occurs when it decrease. Qiu et al. [25] has suggested that this influence of heat generated by exothermic oxidation of CaO explain some observations in virtually 'intraparticle' reaction as they use a very small amount of substance. This becomes much more important when a large amount of substance is involved.

3.1.4. Behaviour of O_2 during oxidation

O_2 reacts with CaS very quickly and the reactor outlet gases contain virtually No O_2 in within a few minutes of oxidation, even when 8% O_2 is used.

Fig. 7 shows the trend over time of the oxygen concentration in the reactor outlet gas when using grain sizes of 2–2.5 mm, 8% O_2 and a gas velocity of 29.11 cm s^{-1} (test 16, Table 3). Plots are shown for 4% O_2 and two gas velocities (29.11 cm s^{-1} (test 11) and 14.55 cm s^{-1} (test 12) are used.

In the first few minutes (more minutes at lower oxygen concentration and lower gas velocity), there is virtually no oxygen in the outlet gas. It is also evident that its content will subsequently increase until it virtually reaches the initial concentration at the end of the tests when SO_2 content is very low (<20 ppm). This is due to the fact that at higher oxygen concentration and higher gas velocity there are more supply of oxygen by time unit, and by this is more difficult for all the oxygen to react and this element will appear earlier in the outlet gases. This may be important when comparing the action of oxygen with other oxidants, such as CO_2 and H_2O, that react more slowly. This is discussed below.

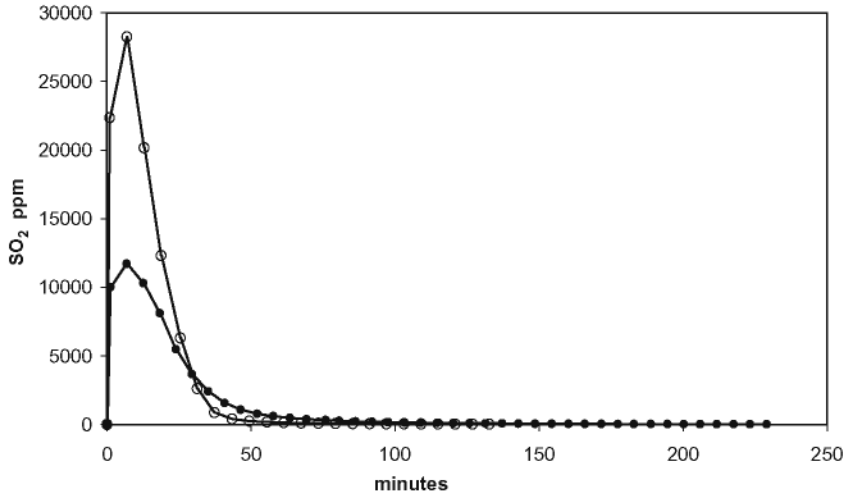

Fig. 6. SO_2 content in the outlet gases at 850 °C, grain size 2–2.5 mm; tests 16 (○: 8% O_2, 29.11 cm s^{-1}) and 11 (●: 4% O_2, 29.11 cm s^{-1}).

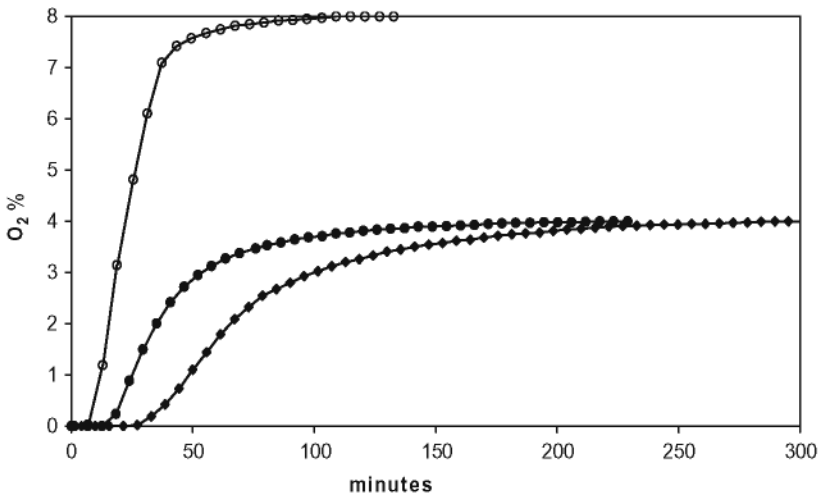

Fig. 7. O_2 trend at 850 °C and grain size 2–2.5 mm; tests 16 (○: 8% O_2, 29.11 cm s^{-1}), 11 (●: 4% O_2, 29.11 cm s^{-1}) and 12 (♦: 4% O_2, 14.5 cm s^{-1}).

3.2. Influence of other oxidant gases: CO_2 and H_2O

3.2.1. Oxidation by CO_2

Anthony et al. [26] established that CO_2 reacts with CaS to produce SO_2 and CO, but little or no COS. To clarify the CO_2 effect, two tests have been carried out: one with CO_2 (21%) and N_2 (test 18, Table 3), and another with CO_2 (17%) and N_2 only at the beginning and later with CO_2, N_2 plus 4% O_2 (test 4).

When only CO_2 (21%) is used (test 18 in Table 3) in a sulphured sample of 2–2.5 mm grain size, 14.55 cm s^{-1} gas velocity and 11 cm bed thickness, the gases emitted over time are shown in Fig. 9. With respect to COS, initially there is great COS release, but this quickly decreases. With respect to SO_2 initially is a little release that initially decreases slowly over time and later increases until a constant level of approximately 1000 ppm is attained.

From the different reactions that can be considered, it is obvious that reaction (4) is initially important but reaction (5) is later dominant. In any case, COS released tends to stabilise around 20 ppm.

There is no clear evidence that reactions (15) and (16) producing calcium carbonate or calcium sulphate take place. The X-ray diffractogram for this sample (Fig. 9) shows no calcium carbonate or calcium sulphate peaks (these products are highly crystalline and readily detected). In the chemical analysis of the end product, the amount of calcium sulphate detected after more than 6 h of treatment is only 0.24%, very low compared to the amount of calcium oxide (8.95%). The peak of this CaO, which is much less crystalline than other compounds considered is easily detected in the diffractogram.

Initially, on the action of CO_2 when 1465 ppm of COS is detected, a minimum amount of CS_2 is also detected by using a DMD detector, a detector specifically for sulphur compounds (this low amount of CS_2 cannot be detected with the commonly used TCD detector). Latter, this peak of CS_2 is less visible when the amount of COS present is 480 ppm and after it cannot be observed. This means that reactions (12) or (13) are possible, bearing in mind that reaction (12) can be considered the sum of reactions (4) plus (13).

The CO_2 concentration used is not a determining factor for this behaviour because the content or concentration of this compound in the initial gas is 21% and little is consumed, which means that the CO_2 concentration is virtually steady al all reacting points and at all times. The most notable difference between the initial and subsequent moments is that the sample surface is initially composed almost entirely of CaS and afterwards CaO is present on the grain surface, at least partially.

This behaviour could be attributed to a chain of reactions: initially, reactions (4) and (12) take place in competition with reaction (5) while only CaS is present on the surface. Later, when CaO has also formed, part of the COS (and CS_2) reacts with CaO to produce new CaS according to the reverse of reaction (4). This newly formed CaS reacts according to (4) and (5) and by successive reactions, the amount of COS produced is notably reduced and tends to steady state. The same occurs with COS released from the inner layers of a grain. This COS must go through outer layers with CaO (this effect is more significant at larger grain sizes) and reacts according to the reverse of reaction (4).

The rate of CaS decomposition due to reaction with CO_2 at 850 °C is very small (Fig. 8). Although it would be possible according to Anthony et al. [26] to completely oxidize CaS because there is virtually no covering or clogging of pores because no calcium carbonate or calcium sulphate is being formed, this would take a long time. In the case considered and assuming a stabilised production of approximately 1000 ppm of sulphur compounds (SO_2 plus COS) at gas velocity of 5 l/min, this is equivalent to 0.0134 mol/h. Since the CaO involved in the test is 0.544 mol (100 g of dolomite), the complete conversion would take 40.6 h (if the release rate does not change).

In test 4 (Table 3), only 17% CO_2 is used for 64 min and 4% O_2 is added afterwards. Under these conditions, the oxidation rate speeds up when oxygen is added to obtain reasonable results within less time and SO_2 release is really noticeable when oxygen is introduced. At the end of the test, residual CaS (0.43%) levels are similar to those for the test with 4% O_2 and 96% de N_2 (test 1; Tables 3 and 4). During the time in which the only oxidant gas was CO_2, SO_2 release stabilises at about 1004 ppm, a very little higher value than in test 18. COS stabilises at around 17 ppm, a little lower than in test 18; however, as the gas velocity in test 4 is actually twice that for test 18 then the sulphur compound release rate in absolute quantities is twice than in test 18 because the content in the outlet gas in both cases is about 1000 ppm. This difference in absolute quantities of SO_2 release rate can be explained by the higher specific surface of the sample with smaller grain size and because the CO_2 molecule is a "relatively" large molecule that does not quickly penetrate by the pores of the outer layer of the grains and by this their reactivity is more influenced by the specific surface of the sample. This difficulty in penetration can be the reason that the CaS conversion rate using only CO_2 is very small and in test

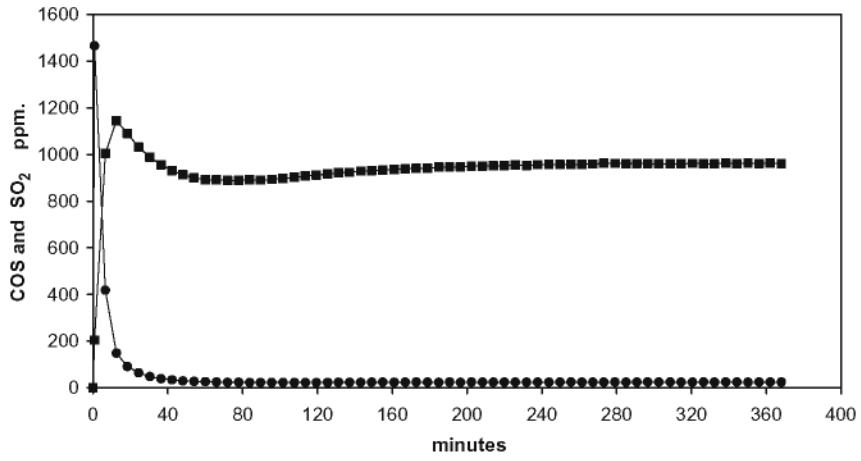

Fig. 8. COS and SO_2 content in the outlet gases during oxidation in test 18: oxidation with 21% CO_2, grain size 2–2.5 mm, 850 °C, COS (●), SO_2 (■).

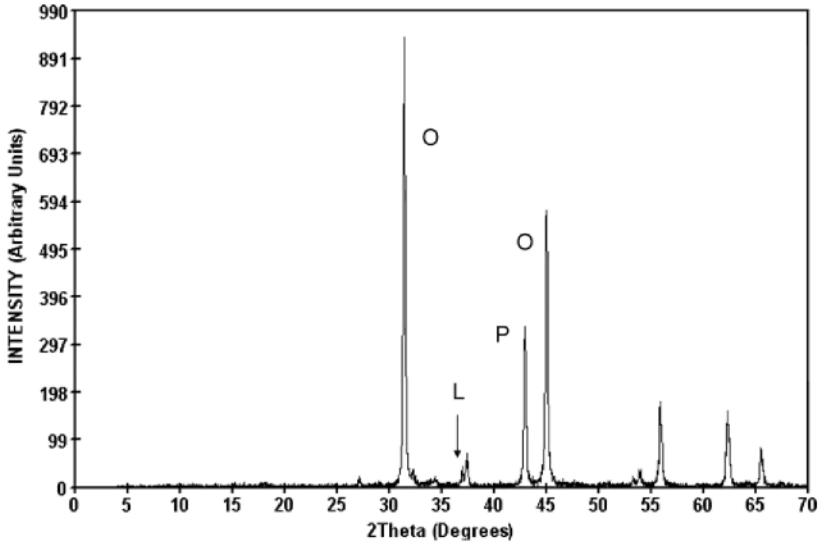

Fig. 9. X-ray diffractogram of the product of test 18; oxidation with 21% of CO_2, 79% N2; L: lime, O: oldhamite, P: periclase.

4 the complete conversion would take about 20 h and in the test 18 would take 40 h (if the release rate does no change at times longer that the used in the tests).

3.2.2. Oxidation by H_2O

Wu [24] found that H_2O vapour can react directly (in absence of oxygen) with CaS and produces SO_2, H_2 and a negligible amount of H_2S and No $CaSO_4$.

Test 10 was performed using only nitrogen and 20% H_2O (for 110 min) and show an initially large release of H_2S that quickly dropped to steady state at about 370 ppm and an initially low release of SO_2 that also tended to reach steady state at approximately 540 ppm (Fig. 10).

Reactions (6) and the reverse of reaction (1) are different ways to oxidise calcium sulphide; one produces SO_2 and the other H_2S. This means that reactions (6) and the reverse of reaction (1) are competing reactions. Where CaO is not present, the reverse of reaction (1) is more important and H_2S is released throughout the entire CaS column because the reaction is not very 'extensive' (unlike what occurs with oxygen) and does not consume all the water vapour introduced, but rather only a very small proportional part. When some CaO has already been formed, H_2S is adsorbed on CaO to restore CaS according to reaction (1). CaS is then oxidised again by H_2O. The result is a drop in the amount of H_2S produced and an increase in SO_2 until steady state is achieved. This steady state is maintained for a long time because oxidation with water under the conditions used is not very active. This phenomenon also occurs inside the grain when H_2S produced inside the grain must go through the previously formed CaO layer.

As occurs with the case of CO_2, during oxidation by water vapour, the oxidation rate is very low under the conditions used (approximately 900 ppm of sulphur compounds are released).

After 110 min, 4% O_2 is introduced (in addition to water vapour) and the oxidation reaction speeds up; 240 min later, oxidation stops (SO_2 concentration in the gas released is 18 ppm) and the chemical analysis gives 38% residual CaS, showing that more pore clogging or covering has occurred. This is important and is further discussed in Section 3.2.3.

3.2.3. Oxidation with a blend of N_2 plus O_2, CO_2 and H_2O

When an exhaust gas released from combustion is used as oxidation gas, nitrogen and oxygen are present along with carbon dioxide and water vapour. To study this case, various tests were carried out with a blend of 13% CO_2, 7% water vapour, 4% O_2 and

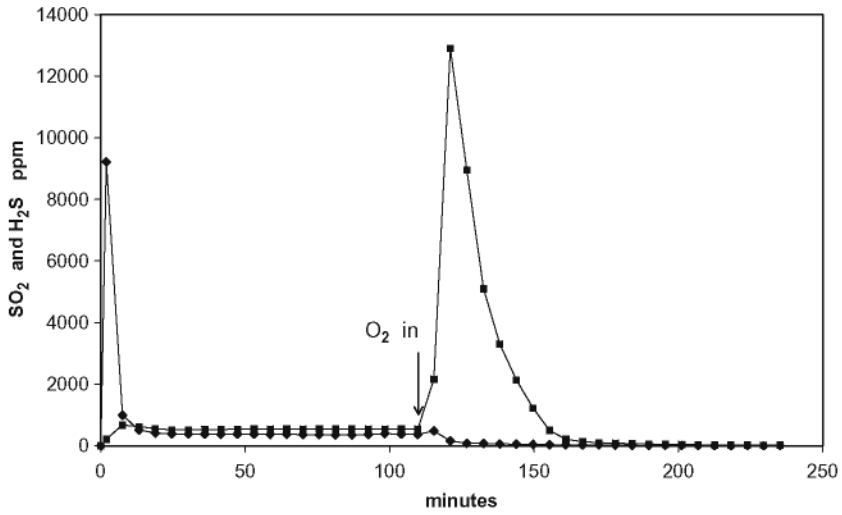

Fig. 10. H_2S and SO_2 trend in test 10 (oxidation with 20% H_2O, grain size 0.71–1 mm, 850 °C) SO_2 (■), H_2S (♦).

76% N_2, using a gas temperature of 850 °C, gas velocity of 29.11 cm s^{-1}, 100 g of dolomite and the three grain sizes mentioned above (tests 2, 7, 8 and 13)

As discussed previously, the presence of CO_2 and H_2O will lead to the formation of COS and H_2S as well as SO_2 and CO. However, these oxidant compounds do no react extensively and are not consumed in the initial CaS bed area and therefore act over the entire length of the bed. Oxygen, by the contrary, is consumed in the first part of the CaS bed and need time to be detected at the end of the bed, especially if the oxygen concentration is not very high. As a result, COS and H_2S initially appears in the outlet gases and tend to disappear in this gas over time for reasons discussed in previous points and also because when appears any oxygen in the lower part of the bed oxidises any COS, CO and H_2S according to reactions (7) and (8). Initially, the Figs. 11 and 12 (test 13, Table 3) show that the H_2S concentration is approximately 1000 ppm and the COS is virtually invisible in this figure because its content is about 5 ppm. Both compound decreases rapidly their presence and practically disappears at 20 min. The low level of COS can be explained by its reaction with the water introduced (9).

The chemical analysis results listed in Table 5 show that residual CaS is higher than in previous cases when only a blend of oxygen and nitrogen is used (all other conditions being equal) as can be seen comparing test 2 in Table 5 with test 1 in Table 4; test 7 in Table 5 with test 6 in Table 4 and test 13 in Table 5 with test 11 in Table 4. The influence of grain size is also more important than when only oxygen is used as an oxidant. CaO content is higher than when only nitrogen and oxygen are used, although the calcium sulphate content is lower.

A comparison was performed with grain size of 0.4–0.5 mm under conditions of oxygen and nitrogen only (test 1 in Table 4) and under conditions of a blend with the same oxygen concentration (4%) but with water vapour and carbon dioxide (test 2 in Table 5). This comparison showed that the CaO content in the product was higher when water and carbon dioxide were used (19.17% vs.14.76%) despite higher residual CaS content (0.83% vs. 0.45%). This finding is not consistent with [25] on this point.

Using higher grain sizes (2–2.5 mm), residual CaS under conditions of a blend with oxygen (4%), water vapour and carbon dioxide is much higher (23.58%, test 13 in Table 5) than when only nitrogen

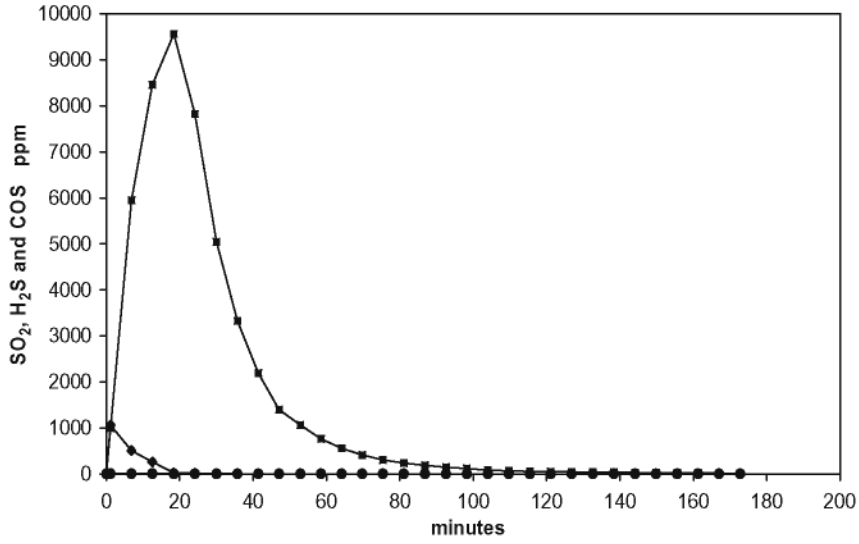

Fig. 11. SO_2, H_2S, and COS trend in test 13 (oxidation mix: H_2O, CO_2 and O_2, grain size 2–2.5mm, 850 °C). SO_2 (■), H_2S (♦), COS (●).

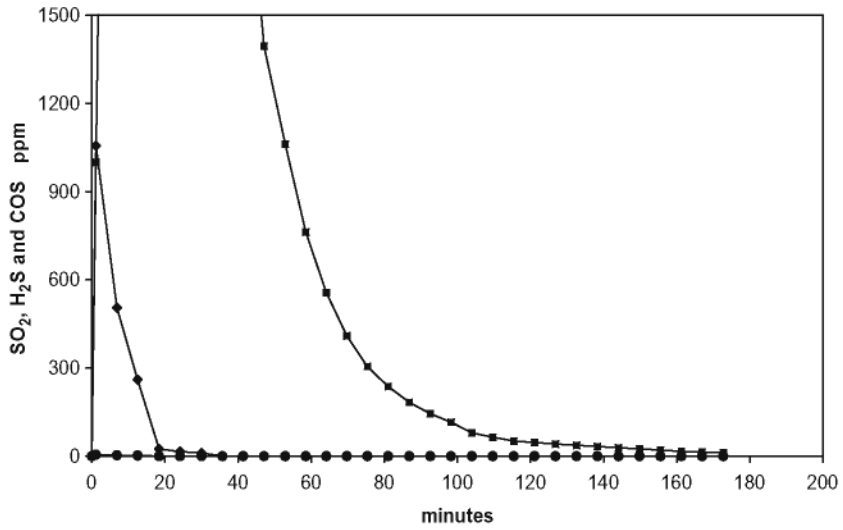

Fig. 12. SO_2, H_2S, and COS evolution in test 13, enlargement of Fig. 12 (oxidation mix: H_2O, CO_2 and O_2, grain size 2–2.5 mm, 850 °C). SO_2 (■), H_2S (♦), COS (●) $12H_2S$.

Table 5
Oxidation with a mix of O_2, 7% H_2O, 13% CO_2 and N_2 as balance gas: influence of grain size and oxygen partial pressure (oxygen content).

Test	Size (mm)	Bed length (cm)	Gas veloc. (cm s^{-1})	O_2 (%)	Tempera. (°C)	CaO (%)	$CaSO_4$ (%)	CaS (%)	$CaO/CaSO_4$
2	0.4–0.5	11.4	29.11	4	850	19.17	50.78	0.83	0.378
7	0.71–1	11.4	29.11	4	850	21.75	44.44	3.26	0.489
13	2–2.5	11.4	29.11	4	850	11.57	33.50	23.58	0.345
8	0.71–1	11.4	29.11	2	850	18.40	46.24	5.46	0.398

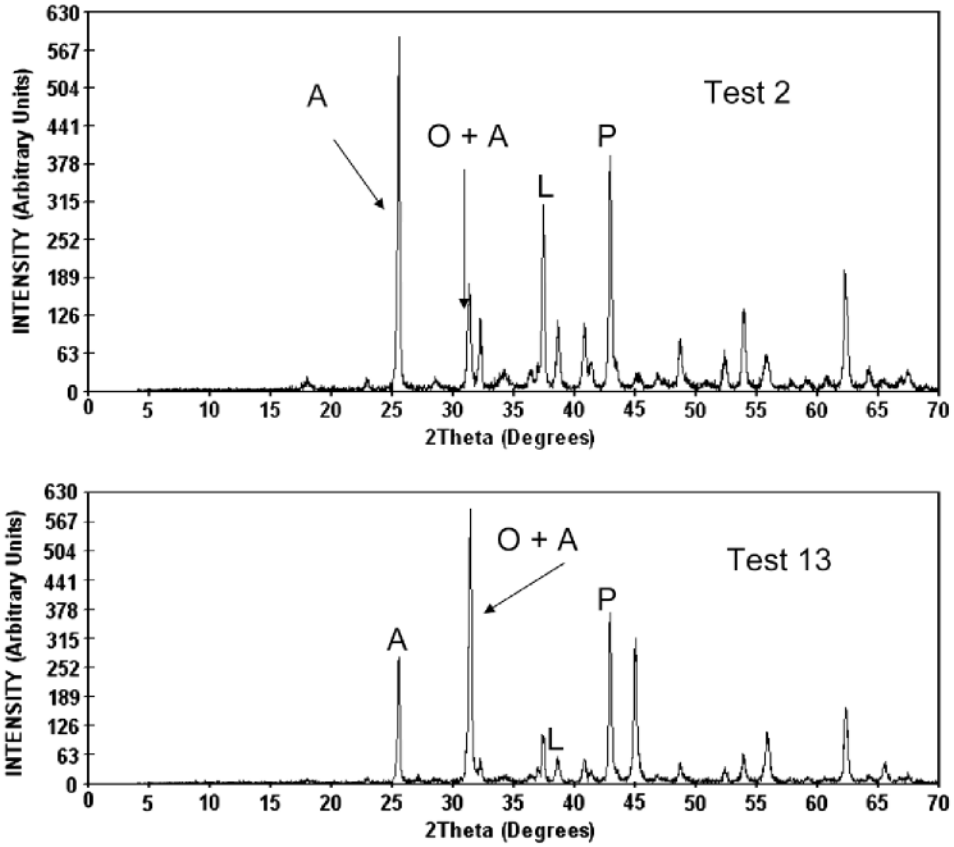

Fig. 13. X-ray difractograms of the oxidation products of tests 2 (0.4–0.5 mm) (in top) and13 (2–2.5 mm) (in bottom), with a mix of 4% O_2, 13% CO_2 and 7% H_2O, 850 °C; A: anhydrite, L: lime, O: oldhamite, P: periclase

and oxygen are used (4.32%, test 11 in Table 4) due to more pore clogging caused by larger grain size. The CaO content is slightly higher than when only nitrogen and oxygen are used (11.57% vs. 10.18%).

The $CaS/CaSO_4$ ratio is higher in all grain sizes when used the mix of water vapour, carbon dioxide and oxygen compared to tests conducted with the same temperature, bed length and gas velocity, but with only N_2 and 4% O_2 (tests 2, 7 and 13 in Table 5 compared respectively with tests 1, 6 and 11 in Table 4).

This contradicts studies by Wu [25] who defended a synergistic action of H_2O and O_2 during CaS oxidation. Wu's study was carried out with a small amount of substance (60 mg). According to that study, water vapour was able to achieve greater penetration; moreover, CaO formation (instead $CaSO_4$) would facilitate oxygen access.

In the present study conducted with a large amount of substance, one explanation is that the innermost pores created by H_2O are used by the oxygen and SO_2 blend previously produced to yield calcium sulphate with CaO. This increased the possibility of earlier, more substantial, pore clogging and will therefore leave more residual CaS.

Fig. 13 shows the X-ray diffractograms of the two extreme cases (test 2 and 13, 0.4–0.5 mm and 2–2.5 mm). The large amount of residual CaS in the case of the larger size is obvious.

Test 9 (Table 3) was carried out using 150 g instead of 100 g, which has little effect on residual CaO as discussed previously. In this test, however, the water vapour content is higher (15.6%) and the carbon dioxide content is lower (7.8%), but the oxygen concentration remains steady (4%) as compared with test 7 (Tables 3 and 5). The results of this test (no shown in the tables) are: Residual CaS: 8.58%, CaO: 20.3% and $CaO/CaSO_4$ ratio 0.508. Residual CaS increases by 8.58% compared with 3.26%, showing the negative effect of water vapour, because carbon dioxide has been reduced. The CaO content is of 20.3% a little lower than in test 7 (21.75%). The $CaO/CaSO_4$ ratio was increased by 0.508, higher than in the test conducted using the same grain size and temperature, but with only 7% water vapour: 0.489 in test 7, Table 5.

4. Conclusions

1. The most efficient oxidant for CaS is O_2. H_2O and CO_2 can also oxidise CaS, but at a much slower rate than O_2.
2. When H_2O vapour is mixed with N_2 and O_2, a higher amount of residual CaS is produced than with the N_2 and O_2 blend alone, but increases CaO content.
3. Grain size is a key parameter for the control of residual CaS under any conditions (fixed bed arrangement) due to problems of pore clogging. The best grain size is the smaller used: 0.4–0.5 mm. In the desulphurisation process is the contrary to obtain the best results, the better grain size is the bigger used 2–2.5 mm because there is not a problem of pore clogging.
4. Higher O_2 concentrations in the oxidation gas produce lower amounts of residual CaS.
5. Less residual CaS is produced at 850 °C than at 700 °C. More $CaSO_4$ conversion, more pore clogging and more residual CaS occurs at a lower temperature.
6. Increased bed length moderately increases residual CaS.
7. CO_2 used alone produces a notable amount of COS and a very small amount of CS_2 at the start of oxidation but these compounds tends to quickly decrease due to a chain of reactions with produced previously CaO and COS tends to be much lower than SO_2 production.
8. Water vapour used alone produces a notable amount of H_2S at the start of oxidation, but the latter compound tends to decrease quickly due to a chain of reactions with previously produced CaO and tends to be equal to SO_2 production.

Acknowledgements

The authors would like to thank the European Commission–DG Research, Research Fund for Coal and Steel (RFC-CR-04006) for supporting this study.

The authors would also like to thank UPM – R05/11205(RFC M0500204145) and UPM – CCG06-UPM/TQ-351 (RFC M0700204178) for supporting this line of investigation of the research group.

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